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Fabrication of High-Quality $SmBa_2Cu_3O_{7-\delta}$ Thin Films by a Modified TFA-MOD Process

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수정된 TFA-MOD법에 의한 $SmBa_2Cu_3O_{7-\delta}$ 박막의 제조

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Abstract

We report a successful fabrication of high-quality $SmBa_2Cu_3O_{7-\delta}$ (SmBCO) thin films on $LaAlO_3$(LAO)(100) single crystalline substrates by a modified TFA-MOD method. After the pyrolysis heat treatment of spin-coated films up to 400℃, SmBCO films were fired at various temperatures ranging from 810 to 850℃ in a reduced oxygen atmosphere (10 ppm O_2 in Ar). Optimally processed SmBCO films exhibited the zero-resistance temperature ($T_{c,zero}$) of 90.2 K and the critical current density (J_c) of 0.8 MA/cm^2 at 77K in self-field. Compared with the J_c values (normally, > 2 MA/cm^2 at 77 K) of MOD-TFA processed YBCO films, rather depressed J_c values in SmBCO films are most probably attributed to the existence of *a*-axis oriented grains.

Keywords : SmBCO, TFA-MOD, critical current density, coated conductor

I. Introduction

Recently, high-J_c $YBa_2Cu_3O_{7-\delta}$ (YBCO) thin films have been prepared by PLD (Pulsed Laser Deposition), PED (Pulsed Electron Beam Deposition), sputtering, co-evaporation, MOCVD, etc. However, since these methods are a high-cost vacuum technology for producing high-temperature superconductors, a simple, scalable, and low-cost process has been favored for real applications. In this respect, the metalorganic deposition using trifluoroacetates (TFA-MOD), which is a non-vacuum technology, is regarded as one of the most promising methods for the commercialization of YBCO coated conductors.

Since Gupta *et al.* [1] announced a successful fabrication of YBCO thin films with the TFA-MOD process in 1988, McIntyre *et al.* [2] have first reported high-J_c values over 1MA/cm^2 at 77K in self-field for YBCO films produced by the TFA-MOD method, and thereafter several other research

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groups achieved high-J_c YBCO films on single-crystalline substrates with this process [3~5]. More recently, high-J_c values have also been obtained from YBCO thin films deposited on various metallic substrates including rolling assisted biaxially textured substrate(RABiTS) [6,7] and ion-beam assisted deposition(IBAD) tape [8~10].

It is well-known that optimally processed LRE $Ba_2Cu_3O_{7-\delta}$ (LRE = La, Nd, Sm, Eu, Gd) bulk superconductors commonly exhibit higher J_c in high magnetic fields at 77 K in comparison with YBCO bulks [11,12]. Therefore, it has been expected that LREBCO films also would represent stronger flux pinning if their processes are optimized. Recently, Honjo *et al.* [13] reported T_c = 89K for a NdBCO film fabricated by using the TFA-MOD method and Iguchi *et al.* [14] reported that the highest value of T_c of these TFA-derived $GdBa_2Cu_3O_{7-\delta}$ (GdBCO) films was 92.9K and their J_c value reached 2.9MA/cm^2 at 77K in self-field. However, there has been no report on SmBCO films produced by the TFA-MOD method although Sudoh *et al.* [15] and Ko *et al* [16]. reported high-J_c values over 1MA/cm^2 for SmBCO films prepared by PLD and PED, respectively, which motivated present study. In this paper, we, for the first time, report successful fabrication of high -quality SmBCO thin films on LAO(100) single crystalline substrates by the TFA-MOD method.

II. Experimental

The precursor solution was prepared by a modified TFA-MOD method. First of all, Sm_2O_3, $BaCO_3$ and CuO (all 99% purity) were weighed to have the cation ratio of Sm:Ba:Cu = 1:2:3, ball-milled for 24 h, and then calcined at 880℃ for 12 h in air. To synthesize a pure SmBCO phase, the calcination step was repeated three times with an intermediate ball-milling. Unlike the normal TFA-MOD method employing metal trifluroacetates, the precursor solution was prepared by dissolving the synthesized SmBCO powder into de-ionized water containing trifluoroacetic acid. The total metal ion concentration in the precursor solution was 1.5 M/L, which was controlled by dissolution of blue gel into methanol. The precursor solution was coated on the LAO(100) single-crystalline substrates with a spin coater. The spin coating was performed for 120 s with a spinning rate of 4000 rpm.

The heat treatment schedules used for fabrication of SmBCO superconducting thin films are schematically illustrated in Fig. 1. At first, as shown in Fig. 1(a), spin-coated films were slowly heated to 400℃ over about 20 h in a 4.2 % humidified oxygen

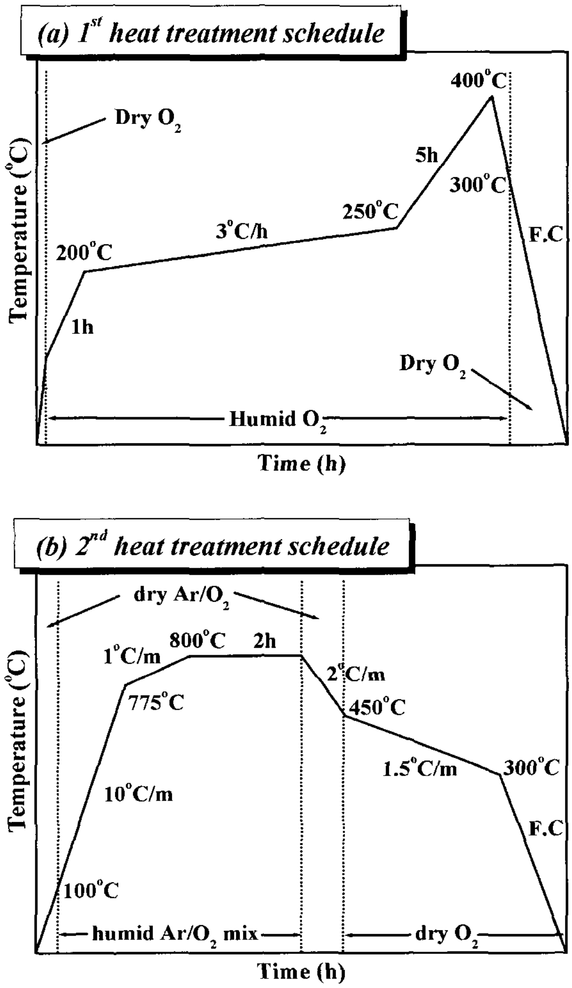

Fig. 1. Schematic illustration of the first heat treatment for the decomposition of organic components (a) and of the second heat treatment for the 123 phase formation (b).

atmosphere with a flow rate of 400 ml/min to form the oxy-fluorides films, and then furnace-cooled. Subsequently, SmBCO films were produced by firing the films in a humid atmosphere containing a mixed gas of 10 ppm O_2 in Ar as shown in Fig. 1(b). Samples were prepared by varying the firing temperature from 810 to 850℃ for 2 h. Silver protecting layers of ~1.5㎛ in thickness were deposited onto the fired SmBCO films using a dc magnetron sputter. After silver deposition, samples were oxygen-annealed at 450℃ for 1 h.

SmBCO films were characterized by X-ray diffraction (XRD) using Cu-Kα radiation. In-plane texture was quantified by measuring the full-width half maximum (FWHM) values of the Φ-scan for (102) peak, and out-of-plane texture (i.e., c-axis alignment) was determined by measuring the FWHM values of the ω-scan of (005) peak as determined by high-resolution X-ray diffraction (HR-XRD). The microstructures of samples were observed by field emission scanning electron microscopy (FE-SEM). The T_c values of samples were measured by the standard four-probe method and their critical currents (I_c) were obtained by measuring the I-V curves at 77K in self-field using 1㎶/cm voltage criterion, and J_c values were estimated from the I_c values.

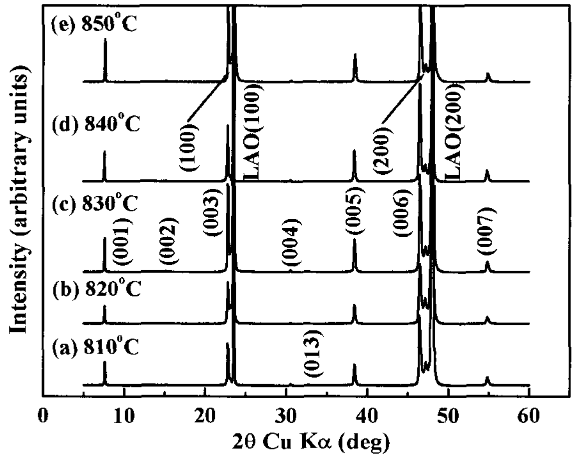

Fig. 2. XRD patterns of SmBCO films on $LaAlO_3$(100) single crystalline substrates prepared at various firing temperatures.

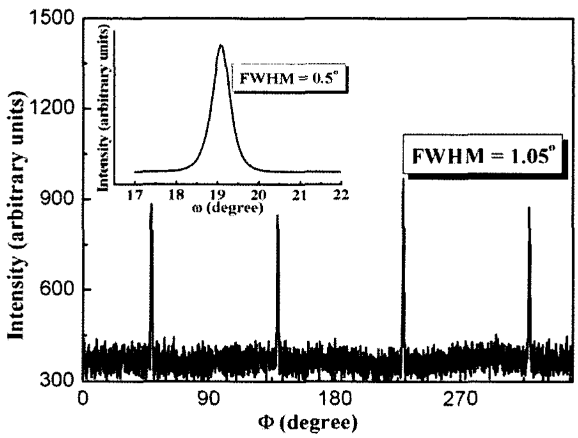

Fig. 3. (102) Φ-scan of the SmBCO thin film fired at 840℃ for 2 h. The inset is (005) ω-scan of this film.

III. Results and Discussion

Figure 2 shows θ-2θ XRD patterns of the SmBCO films on LAO(100) single crystalline substrate fired at various high temperatures. Well developed (00l) peaks indicate that all these films are highly c-axis oriented. However, the sample fired at 810℃ shows a small (013) peak, representing some random-oriented grains. Small peaks due to the existence of a-axis oriented grains are commonly observed for all samples, as indicated by the (100) peak at 23.12° and (200) peak at 47.20°. The existence of a-axis oriented gains in TFA-MOD processed YBCO films are known to be very detrimental to the supercurrent flow, thus greatly suppressing the J_c.

In-plane and out-of-plane textures of the SmBCO films were characterized by the FWHM values of X-ray Φ and ω-scan, respectively. All samples showed a four-fold symmetry in their Φ-scans. As a representative, the data for the SmBCO film fired at 840℃ are displayed in Fig. 3. The FWHM values of the (102) Φ-scan and (005) ω-scan were approximately 1.05° and 0.5°, respectively. With the firing temperature increased from 810 to 840℃, the FWHM values of (005) ω-scan monotonously decreased from 0.55° to 0.5° and then increased to 0.66° at 850℃. For the (102) Φ-scan, however, the

FWHM values were almost unaltered.

Surface morphologies of SmBCO films observed by FE-SEM are shown in Fig. 4. In this figure, needle-shaped grains represent *a*-axis (and/or *b*-axis) oriented grains while flat surfaces with hills and pores indicate *c*-axis oriented grains. The samples fired at temperatures lower than 840℃ have a large amount of *a*-axis oriented grains and pores. With increase of the firing temperature, however, the amount of *a*-axis oriented grains is gradually reduced in the films.

Figure 5 shows the $T_{c,\text{zero}}$ and the transition width ΔT_c (= $T_{c,\text{onset}} - T_{c,\text{zero}}$) of the samples. It can be shown that the SmBCO films fired at this firing temperature region exhibit $T_{c,\text{zero}}$ values above 88 K and a sharp transition with ΔT_c values of 0.6~1.8K. More precisely, $T_{c,\text{zero}}$ is found to increase while ΔT_c is decreased as the firing temperature increases up to 840℃, and then the transition behavior becomes worse at the firing temperature of 850℃. These high T_c values are attributed to effective suppression of the Sm^{3+} substitution on the Ba^{2+} site in the $Sm_{1+X}Ba_{2-X}Cu_3O_{7-\delta}$ solid solution.

The *I-V* curve measured at 77 K for the SmBCO film fired at 840℃ is shown in Fig. 6. When the sample width was taken into account, the critical current I_c of this sample was 12 A/cm–width, which in turn corresponded to the J_c value of 0.8 MA/cm^2.

Within our knowledge, this J_c value is a record-high one ever reported for the SmBCO films prepared by the TFA-MOD method. On the other hand, samples fired at 810 and 820℃ exhibited negligible J_c values at 77 K. With increase in the firing temperature from 830 to 840℃, however, the

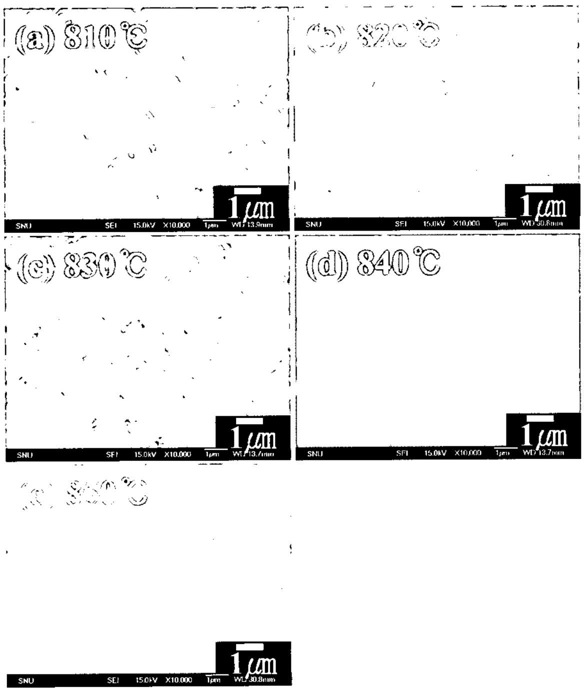

Fig. 4. Surface morphologies of SmBCO films on $LaAlO_3$ (100) single crystalline substrates prepared at various firing temperatures.

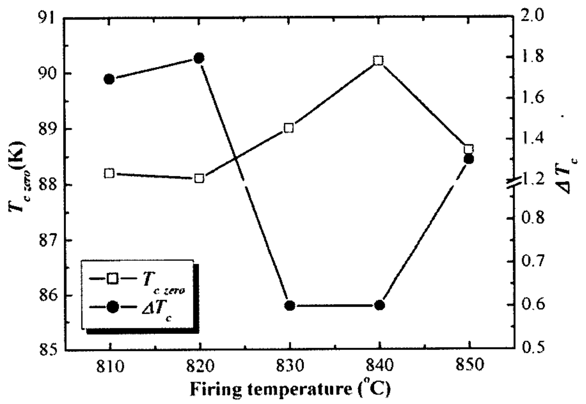

Fig. 5. T_c values of the SmBCO films fired at various temperatures ranging from 810 to 850℃.

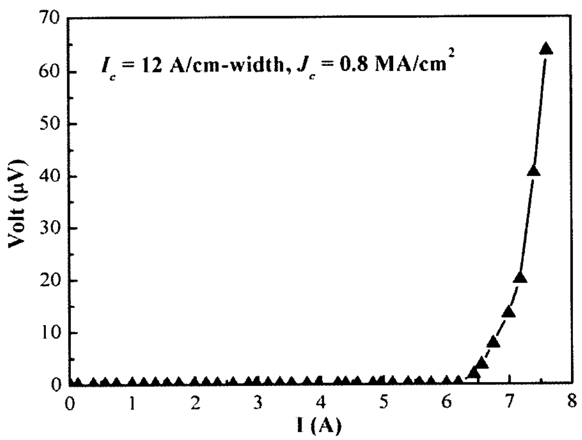

Fig. 6. *I-V* curve at 77 K for the SmBCO film fired at 840℃ for 2 h.

J_c values increased from 0.2 to 0.8 MA/cm^2, and then decreased again to 0.3 MA/cm^2 at 850℃. This variation in the J_c is primarily related to the microstructural features as shown in Fig. 4 and secondly to the superconducting transition behavior represented in Fig. 5.

IV. Summary

In this study, high-quality SmBCO thin films could be successfully fabricated on LAO(100) single crystalline substrate by a modified TFA-MOD method using SmBCO powder as precursor materials. An optimally processed SmBCO sample exhibited the highest T_c of 90.2 K and the largest J_c of 0.8 MA/cm^2 at 77K in self-field. Compared with the J_c values (normally, > 2 MA/cm^2 at 77 K) of TFA-MOD processed YBCO films, rather depressed J_c values in SmBCO films are most probably attributed to the existence of *a*-axis oriented grains. Consequently, it must be crucial to effectively suppress the growth of *a*-axis oriented grains to further improve the J_c of TFA-MOD processed SmBCO.

Acknowledgments

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